THE DEVELOPMENT AND ASSESSMENT OF ORGANOBENTONITE COMPOSITE MATERIALS FOR USE IN THE REMOVAL OF ORGANOCHLORINE PESTICIDES IN WATER

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Specially for my beloved dad, mum, Siaw Fung, Siaw Ai and Chon Lung

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ABSTRACT

This work describes the modification of bentonite to organobentonites in order to change its property from hydrophilic to organophilic to enhance its capability in adsorbing organochlorine pesticides from water. Bentonite was modified by adding quarternary ammonium cations through an ion exchange technique. The organochlorine pesticides studied were heptachlor, aldrin, dieldrin, DDT and mirex. The modified bentonites were characterized using Fourier transform infrared (FTIR), X-ray diffraction (XRD), carbon, and hydrogen and nitrogen analyzer (CHN). Gas chromatography-mass selective detector (GC-MSD) was used to determine the concentration of organochlorine pesticides while evaluating the efficiencies of organobentonites in removing the pesticides from water. Bentonite modified with dodecyltrimethylammonium (DDTMA) has the highest capacity in removing pesticides. DDTMA-bentonite with the lowest amount of quarternary ammonium cations (0.710%) was capable of removing very high percentage of pesticides (95.96±2.50% of aldrin) after 30 minutes of water treatment duration. The optimized treatment conditions of 30 minutes of treatment duration, 0.2000 g of DDTMA-bentonite and 50 rpm of shaking speed were applied throughout this work on the samples obtained from the locations suspected of containing organochlorine pesticides.

ABSTRAK

Penyelidikan ini menerangkan pengubahsuaian bentonit menjadi organobentonit untuk menukarkan sifat bentonit daripada hidrofilik kepada organofilik supaya boleh menambah keupayaan bentonit menyerap pestisid yang bersifat organoklorin daripada air. Bentonit diubahsuai dengan menambahkan kation kuarterner ammonium melalui teknik pertukaran ion. Pestisid berorganoklorin yang dikaji adalah heptachlor, aldrin, dieldrin, DDT dan mirex. Pencirian bentonit terubahsuai dilakukan dengan menggunakan spektroskopi Fourier transform inframerah (FTIR), pembelauan sinar-X (XRD), dan penganalisis karbon, hidrogen dan nitrogen (CHN). Kromatografi gas-pengesan pemilihan jisim (GC-MSD) digunakan untuk menentukan kepekatan pestisid yang bersifat organoklorin dalam proses menilai kecekapan organobentonit menyingkirkan pestisid tersebut daripada air. Bentonit yang diubahsuai dengan dodesiltrimetilammonium (DDTMA) mempunyai kapasiti tertinggi dalam penyingkiran pestisid. DDTMA-bentonit yang mempunyai jumlah kation kuarterner ammonium terendah (0.710%) dapat menyingkirkan lebih banyak pestisid (95.96±2.50% of aldrin) selepas perawatan air selama 30 minit. Keadaan rawatan air yang optimum iaitu masa rawatan air selama 30 minit, DDTMA-bentonit sebanyak 0.2000 g dan kadar pengacauan 50 rpm telah digunakan dalam kajian ke atas sampel yang dikumpul dari kawasan yang berkemungkinan mengandungi pestisid berorganoklorin.

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LIST OF ABBREVIATIONS/SYMBOLS

AAS	-	Atomic absorption spectroscopy
BTEA	-	Benzyltriethylammonium
BTEAB	-	Benzyltriethylammonium-bentonite
BTMA	-	Benzyltrimethylammonium
BTMAB	-	Benzyltrimethylammonium-bentonite
CEC	-	Cation exchange capacity
DDT	-	Dichloro-Diphenyl-Trichloroethane
DDTMA	-	Dodecyltrimethylammonium
DDTMAB	-	Dodecyltrimethylammonium-bentonite
DO	-	Dissolved Oxygen
DTMA	-	Decyltrimethylammonium
DTMAB	-	Decyltrimethylammonium-bentonite
etc	-	Et cetera
FTIR	-	Fourier transform infrared spectrophotometry
g	-	Gram
GCMSD	-	Gas chromatography-mass selective detector
HDTMA	-	Hexadecyltrimethylammonium
HDTMAB	-	Hexadecyltrimethylammonium-bentonite
I.D.	-	Internal diameter
ICP-MS	-	Induced couple plasma-mass spectroscopy
kg	-	Kilogram
m/*z*	-	Mass-to-charge ratio
m	-	Meter
M	-	Molar
meq	-	Milliequivalents of charge
mg	-	Milligram
mg/L	-	Milligram per liter
mL	-	Milliliter
mM	-	Millimolar

ng	-	Nanogram
NMR	-	Nuclear magnet resonance
NTU	-	Nephelometric Turbidity Units
pg	-	Picogram
ppb	-	Part per billion
ppm	-	Part per million
RB	-	Raw bentonite
RM	-	Ringgit Malaysia
rpm	-	Revolutions per minute
R^2	-	Coefficient of determination
SEM	-	Scanning electron microscopy
TDTMA	-	Tetradecyltrimethylammonium
TDTMAB	-	Tetradecyltrimethylammonium-bentonite
TEA	-	Tetraethylammonium
TEAB	-	Tetraethylammonium-bentonite
TGA-DTG	-	Thermal gravimetry analysis-differential thermal gravimetry
XRD	-	X-ray diffraction
µg/L	-	Microgram per liter
	-	Quarternary ammonium cation
	-	Organochlorine pesticide

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CHAPTER I

INTRODUCTION

1.1 Research Background

This research is able to enhance current water treatment process in order to attain better water quality for consumption by adding modified bentonite to remove organochlorine pesticides. During the 7th Malaysia Plan (RMK7), the Government has implemented programmes and efforts to improve environmental health by establishing the Environmental Health Research Centre in September 1997 to cater for the needs of a safe and healthy environment. This is in line with the aspiration of the National Water Resource Council in 1998 to provide an integrated approach for the planning and management of water resources until the year 2050.

The improved, efficient and economic composite materials developed from natural clay materials such as bentonite is prepared by modifying the active sites as well as impregnating them with active cations (In this research, quarternary ammonium cations have been used as the active cations). The increasing presence of organic pollutants in natural water makes the quest for new sorbents an interesting research for the remediation of polluted waters (Piver, 1992). Therefore, the composite materials are useful to remove persistent organic pollutants (POPs) from the water.

Inorganic clays have been shown to sorb numerous polar pesticides (Cox, *et al*., 1994; Cox, *et al*., 1995; Hermosin, *et al*., 1991; Laird, 1996; Celis, *et al*., 1997) and they have been recently suggested as sorbents to eliminate pesticides from water (Gonzalez-Pradas, *et al*., 1993; Gonzalez-Pradas, *et al*., 1996). The organoclays have been found

useful for removing mainly non polar organic contaminants (Boyd, *et al*., 1988) and as well some polar organic contaminants from water (Bottero, *et al*., 1994; Feldkamp and White, 1978; Hermosin and Cornejo, 1992).

The development and evaluation of new materials for the sorption of organic contaminants still remain in the focus of innovative applications in water treatment (Gavaskar, *et al*., 1998; EPA, 1998). The potential of using natural zeolites and clays modified by cationic surfactants for the removal of organic contaminants from aqueous solution was studied by several investigators (Cadena and Cazares, 1996; Li, *et al*., 2000; Li, *et al*., 1998; Li, *et al*., 1999; Haggerty and Bowman, 1994; Boyd, *et al*., 1988; Koh and Dixon, 2001; Gitipour, *et al*., 1997). The natural and modified clay with expandable layered structure is one of the sorbents that attract the present interest of researchers in doing further research on it (Lagaly, 1994).

In 2001, Huttenloch, *et al*. had demonstrated the efficiency of the surface modification of natural diatomite and zeolite material by chlorosilanes. They used trimethylchlorosilane (TMSCl), *tert*-butyldimethylchlorosilane (TBDMSCl), dimethyloctadecylchlorosilane (DMODSCl), and diphenyldichlorosilane (DPDSCl) to possess different headgroups and chemical properties. The surfaces of modified materials in the studies of Huttenloch, *et al.* showed great stability even when exposed to extremes in ionic strength, pH, and to pure organic solvents. The sorption of toluene, *o*-xylene, and naphthalene form water was greatly enhanced by the surface modification. The performance of the enhanced sorption depends on the organic carbon content as well as on chemical characteristics of the chlorosilanes used.

A natural clay material, bentonite was used because it is cheap, easy to obtain as well as having a very good adsorption ability. For example, a 50 pound package of raw bentonite imported from United States of America was RM 50 (purchased in year 2002) whereas only 0.2000 g of the bentonite is needed for removing 10 ppm of organochlorine pesticides as done in the laboratory test run. Moreover, the raw bentonite can also be obtained from our neighbour country such as Indonesia. Organobentonite is bentonite modified by cationic surfactants such as quarternary ammonium cations or similar long-chain molecules to increase their ability to adsorb organic contaminants from aqueous solution (Boyd, *et al*., 1988; Koh and Dixon, 2001)

and contaminated soils (Gitipour, *et al*., 1997). Organobentonite is very useful for the removal of organic pollutants such as organochlorine pesticides. These persistent organic pollutants are found to be very low in concentrations in drinking water. Nonetheless, the persistent organic pollutants are extremely harmful to health since they can bioaccumulate and non-degradable over decades.

Quarternary ammonium cations are used to modify bentonite from hydrophilic to hydrophobic in order to remove organochlorine pesticides which are hydrophobic (Bolto, B. *et al*., 2000). According to Smith, *et al*., 1990, quarternary ammonium cations can be added to the outer and interlayer surfaces of an expandable clay particle by an ion-exchange process and are not easily displaced by smaller cations such as H^+, Na^+, or Ca^{2+}. The enhanced sorption capacity of zeolite materials after modification with hexadecyltrimethylammonium (HDTMA) was shown for benzene, toluene, ethylbenzene and xylene (BTEX) compounds (Cadena and Cazares, 1996), for benzene, aniline, and phenol (Li, *et al*., 2000) and for perchloroethylene (PCE) (Li and Bowman, 1998). Moreover, the removal of inorganic oxyanions such as sulfate, chromate, and selenate from aqueous solution by HDTMA modified zeolite was studied (Haggerty and Bowman, 1994). However, Li *et al.* (Li, *et al*., 1999) proposed a combination of a reductive material (zerovalent iron) with a sorptive material represented by HDTMA-modified zeolites to enhance the removal of chromate and PCE from contaminated groundwater.

The organobentonites that are effective in the removal of organochlorine pesticides from water is suggested to be used in water treatment plants or industries which large amount of water need to be purified.

1.2 Bentonite

The data obtained from technical data sheet of Wyoming bentonite shown that bentonite is an expandable aluminosilicate clay mineral with a unit layer formula of $(Na, Ca)_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2 \cdot nH_2O$. It is a hydrous aluminum silicate comprised principally of the clay mineral montmorillonite which contains small portions of feldspar, calcite and quartz. A montmorillonite mineral is of lamellar shape with a size of

approximately 100 × 100 × 1 nm^3 (Ichikawa, *et al*., 2001). Bentonite is alkaline with a pH range of 8.5 to 10.5.

The clay minerals (such as bentonite, montmorillonite) consist of inorganic aluminosilicate layers carrying negative permanent charge, which is balanced by the hydrated inorganic cations in the interlayer (Socias-Viciana, *et al*., 1998). Bentonite is a 2:1 type of lamellar clay mineral, and its unit layer structure consists of one Al^{3+} octahedral sheet placed between two Si^{4+} tetrahedral sheets (Hillel, 1980, Güngör and Karaoğlan, 2001). The isomorphous substitution of Al^{3+} for Si^{4+} in the bentonite tetrahedral layer results in a net negative surface change on the clay. The ion exchange of Mg^{2+} for Al^{3+} in the structure of octahedral layer also brings to a net negative surface charge on the bentonite (Shen, 2002). Because of the net negative charges, clay minerals have a strong affinity for cations (Li and Bowman, 2001). This charge imbalance is offset by exchangeable cations (typically H^+, Na^+ and Ca^{2+}) on the external and internal surfaces of the clay crystals (Rožić, *et al*., 2000). In aqueous systems, water is intercalated into the interlamellar space of the bentonite, resulting in swelling of the mineral (Smith and Galan, 1995). This interlayer space is available to host polar organic molecules (Mortland, 1970) or organic cations that may substitute the original inorganic ones (Lagaly, 1994; Lagaly and Weiss, 1969); these last organic cation saturated samples are the organoclays.

The structure of bentonite is shown in Figure 1.1 (Terence, 2003).

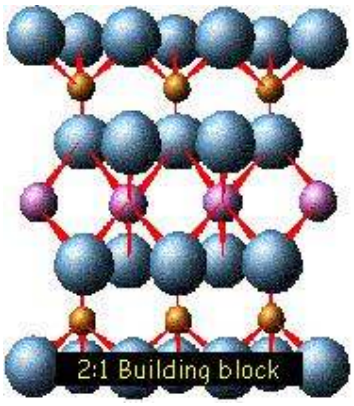


Figure 1.1 The structure of bentonite.

Figure 1.2 shows the Al^{3+} octahedral structure unit. Figure 1.3 shows the Si^{4+} tetrahedral structure unit.

Figure 1.2 Al^{3+} octahedral structure unit.

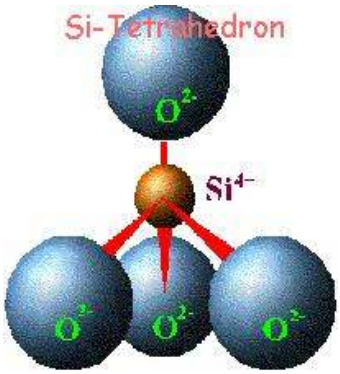


Figure 1.3 Si^{4+} tetrahedral structure unit.

Bentonite can adsorb odor of cat litter, made into facial mask and etc. Some people consume bentonite to help in the adsorption of toxic elements in their body. In this research, the adsorption ability of bentonite is modified from hydrophilic to hydrophobic in order to adsorb the organochlorine pesticides from water.

1.3 Organochlorine Pesticides

Aldrin, dieldrin, DDT, heptachlor and mirex are the organochlorine pesticides to be eliminated from water samples using organobentonites. All of these pesticides

contain chlorine in their structures. Therefore, they are named organochlorine pesticides as well.

The mentioned pesticides are grouped as persistent organic pollutants (POPs) according to their characteristics such as toxicity, persistent (not degradable even after years or decades), mobile (can spread far away from its source through atmosphere by repetition of volatilization and deposit processes), bioaccumulate and bioconcentrate. The uses, characteristics, structures, hydrophobicity and health effects of each organochlorine pesticide are mentioned separately as in the following text.

1.3.1 Aldrin

Aldrin is a white crystalline solid, odourless, with a melting point of 104.0 °C - 104.5 °C (Mercier, 1981). The structure of aldrin is shown in Figure 1.4.

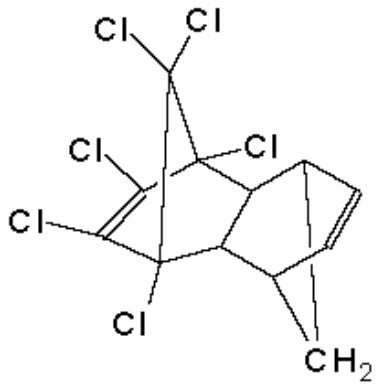


Figure 1.4 The structure of aldrin.

Aldrin is a type of pesticide used to control soil insects including termites, corn root worms and grasshoppers. It had been widely used to protect crops such as corn and potatoes, and had been effectively used in the protection of wooden structures from termites. Aldrin is readily metabolized to dieldrin by plants and animals. It strongly binds to soil particles and is very resistant to leaching into groundwater. However, volatilization is an important mechanism of losing aldrin/dieldrin from the soil. Aldrin is known to be bioconcentrated, mainly as its conversion products, due to its persistent

nature and hydrophobicity. Since aldrin can be rapidly converted to dieldrin in the environment, the fate of these two pesticides can be linked closely (Jones, 1998).

1.3.2 Dieldrin

Dieldrin forms white odourless crystals of melting point 175 °C – 176 °C (Mercier, 1981). Dieldrin was used in agriculture in the control of soil insects and several insect vectors of disease. Nowadays, it has been banned in a number of countries due to environmental and human health concerns.

The half-life of dieldrin in temperate soils is approximately 5 years. This persistence, combined with high lipid solubility, provides the necessary conditions for dieldrin to bioconcentrate and biomagnify in organisms. One of the bioconcentrated methods of dieldrin is by aquatic organisms. The chemical properties of dieldrin (low water solubility, high stability, and semi-volatility) encourage its long range transport (mobility). Similar to aldrin, dieldrin also binds strongly to soil particles and is very resistant to leaching into groundwater. Volatilization is an important mechanism of loss from the soil (Jones, 1998). Dieldrin has been detected in the air, water and organisms including humans and human breast milk (Halsall, *et al*., 1998).

As aldrin is readily and rapidly converted to dieldrin in the environment and in organisms, the levels of dieldrin detected will likely reflect the total concentrations of both compounds. The structure of dieldrin is shown in Figure 1.5.

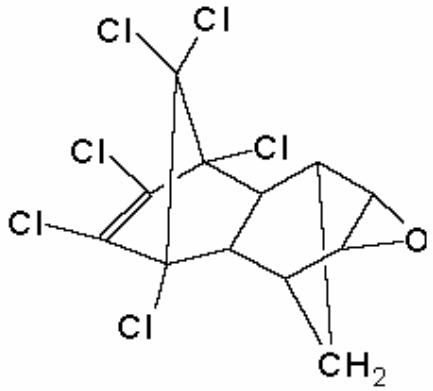


Figure 1.5 The structure of dieldrin.

1.3.3 Dichloro-Diphenyl-Trichloroethane (DDT)

Dichloro-Diphenyl-Trichloroethane (DDT) was commonly used during the Second World War to protect the troops and civilians from malaria, typhus and other vector borne diseases (Bidleman, and Falconer, 1999). After the war, DDT was widely used on a variety of agricultural crops and for the control of disease vectors as well. Growing concern about adverse environmental effects, especially on wild birds, led to severe restrictions and bans in many developed countries in the early 1970s (Ockenden, *et al*., 1998a). Moreover, the ban for DDT is contentious since tropical countries still use DDT to control malaria (Bidleman, and Falconer, 1999). Spencer, *et al.* (1996) had found DDT residues in air above soil at a California farm, where DDT had been applied 23 years previously.

DDT is highly insoluble in water but is soluble in most organic solvents. It is semi-volatile with the ability to partition into the atmosphere. Its presence is ubiquitous in the environment. It is lypophilic and can be stored in the fat of all living organisms. DDT is bioconcentrated in nature. The breakdown products of DDT: 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD or TDE) and 1,1-dichloro-2,2bis(4-chlorophenyl)ethylene) (DDE), are present in the environment and are more persistent than the parent compound. In conclusion, the persistency of DDT and related compounds in the environment is as much as 50% can remain in the soil ten years to fifteen years after application.

The chemical properties of DDT (low water solubility, high stability and semi-volatility) encourage its long range transport. DDT and its metabolites have been detected in arctic air, water and organisms. This route is likely the greatest source of DDT exposure for the general population (Halsall, *et al*., 1998; Ockenden, *et al*., 1998a). Figure 1.6 shows the structure of DDT.

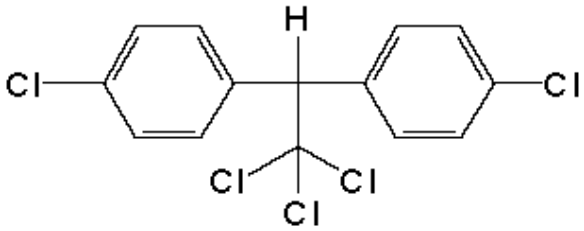


Figure 1.6 The structure of DDT.

1.3.4 Heptachlor

Heptachlor is an insecticide used primarily against soil insects and to combat malaria. Heptachlor is highly insoluble in water but is soluble in organic solvents. It is semi-volatile and able to partition into the atmosphere. It binds readily to aquatic sediments and bioconcentrates in the fat of living organisms. Heptachlor metabolized to heptachlor epoxide whose toxicity is similarly to that of heptachlor, and stored in animal fat (Ockenden, *et al*., 1998b).

The half life of heptachlor in temperate soil is up to two years. This persistence provides the necessary conditions for heptachlor to bioconcentrate in organisms. The chemical properties of heptachlor (low water solubility, high stability, and semi-volatility) favor its long range transport (Jones, 1998). Moreover, heptachlor and its epoxide have been detected in arctic air, water and organisms. WHO suggests that food is the major source of exposure of heptachlor to the general population. The structure of heptachlor is shown in Figure 1.7.

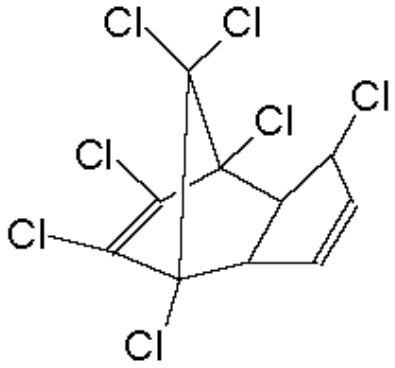


Figure 1.7 The structure of heptachlor.

1.3.5 Mirex

Mirex is an insecticide with little contact activity. Its main use was against fire ants in the southeastern United States, and combat leaf cutters in South America, harvester termites in South Africa. It has also been used as a fire retardant in plastics, rubber, paint paper and electrical goods (Reid, *et al*., 1998). Figure 1.8 is the structure of mirex.

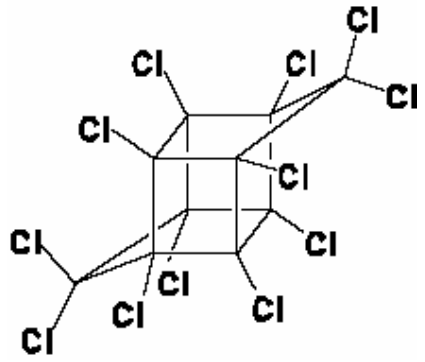


Figure 1.8 The structure of mirex.

Mirex is one of the most stable and persistent pesticides with a half-life of up to 10 years. This persistence, combined with lypophilicity, provides the conditions for mirex to bioconcentrate in organisms. Mirex binds strongly to aquatic sediments due to its insolubility. The chemical properties of mirex (low water solubility, high lipid solubility, high stability, and semi-volatility) favor its long range transport, and therefore, mirex has been detected in arctic freshwater and terrestrial organisms. The main route of exposure of mirex to the general population is through food, especially meat and fish (Jones, 1998, Reid, *et al*., 1998).

1.3.6 Health effects of POPs

A number of persistent organic pollutants (POPs) are available in this research, such as aldrin, dieldrin, DDT, heptachlor and mirex. Table 1.1 shows the health effect of the POPs (Albanis and Hela, 1995; Fatoki and Awofolu, 2003).

Table 1.1: The health effects of POPs.

POPs	Heptachlor	Aldrin/Dieldrin	DDT	Mirex
Health effect	~ Dizziness ~ Fainting ~ Convulsions ~ Mild liver changes ~ Kidney damage ~ Nervous system damage	~ Headaches ~ Irritability ~ Vomiting ~ Uncontrollable muscle movements ~ Convulsions ~ Nervous system damage ~ Kidney damage ~ Death	~ Nervous system damage ~ Excitability ~ Tremors ~ Seizures ~ Irritation of eyes, nose, throat ~ Changes of liver enzymes	~ Nervous system damage ~ Reproductive system damage ~ Liver damage ~ Harm development in rodents ~ Miscarriage

The LD50 is a standardized measure for expressing and comparing the toxicity of chemicals. The LD50 is the dose that kills half (50%) of the animals tested (LD = "lethal dose"). The animals are usually rats or mice, although rabbits, guinea pigs, hamsters, and so on are sometimes used. Ritter, *et al*. (1999) has shown the toxicity (LD50) of the studied persistent organic pollutants including aldrin, dieldrin, heptachlor, DDT and mirex in their report which as the following.

The acute oral LD50 for aldrin in laboratory animals is in the range of 33 mg/kg body weight for guinea pigs to 320 mg/kg body weight for hamsters. Reproductive effects in rats were observed when pregnant females were dosed with 1.0 mg/kg aldrin subcutaneously. In laboratory studies, acute oral LD50 values in the range of 37 mg/kg body weight in rats to 330 mg/kg in hamsters have been found for dieldrin. Dieldrin residues have been detected in air, water, soil, fish, birds and mammals, including humans and human breast milk. As aldrin is readily and rapidly converted to dieldrin in the environment and in organisms, the levels of dieldrin detected likely reflect the total concentrations of both compounds.

The acute oral LD50 of heptachlor to laboratory animals is in the range of 40 mg/kg body weight in rats to 116 mg/kg in rabbits. A daily intake of 0.25 µg/person/day

(for heptachlor and heptachlor epoxide combined, based on a 60 kg person) was estimated for Vietnam, and of 0.07 μg/person/day (for heptachlor alone) for India.

DDT and related compounds are very persistent in the environment, as much as 50% can remain in the soil 10-15 years after application. DDT has also been detected in human breast milk. In a general survey of 16 separate compounds in the breast milk of lactating mothers in four remote villages in Papua, New Guinea, DDT was detected in 100% of forty-one samples taken. DDT is not highly acutely toxic to laboratory animals, with acute oral LD50 values in the range of 100 mg/kg body weight for rats to 1770 mg/kg for rabbits. DDT is highly toxic to fish, with 96-hour LC50 values in the range of 0.4 μg/L to 42 μg/L.

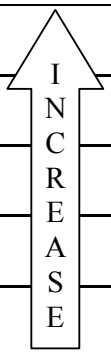
In acute studies, the oral LD50 of mirex to rats ranges from 600 to >3000 mg/kg, depending on sex of the test animal and nature of the formulation tested. Short term effects included decreased body weight, hepatomegaly, induction of mixed function oxidases, and morphological changes in liver cells.

1.3.7 Hydrophobicity of POPs

It is important to know the hydrophobicity of the POPs because the hydrophobicity of modified bentonite should suit with that of the organochlorine pesticides in order to adsorb the pollutants (Cadena, 1989). The amount of chlorine found in the structure of the organochlorine pesticides is one of the criteria to determine their hydrophobicity. In this research, quarternary ammonium cations with different amount of carbon atoms (short alkyl or aryl group and long alkyl group) give different hydrophobicity to the modified bentonite. The hydrophobicity matching between organochlorine pesticides and modified bentonite is evaluated through the results of laboratory test run on the capability of modified bentonite in removing the organochlorine pesticides. In other words, higher percentage of certain organochlorine pesticide will be removed by the particular modified bentonite which its hydrophobicity is matched. Table 1.2 shows the hydrophobicity of POPs.

Table 1.2: The hydrophobicity of POPs.

PESTICIDES	WATER SOLUBILITY	HYDROPHOBICITY
Mirex	Insoluble	
DDT	1.2-5.5 µg/L at 25 °C	
Dieldrin	140 µg/L at 20 °C	
Aldrin	17-180 µg/L at 25 °C	
Heptachlor	180 µg/L at 25 °C	



1.4 Quarternary Ammonium Cations

A range of cationic surfactants mainly primary and quarternary alkylammonium have been use to render different organoclays (Dentel, *et al*., 1995; Hermosin, *et al*., 1995; Mortland, *et al*., 1986; Zhang, *et al*.,1993). Therefore, modification of bentonite from hydrophilic to hydrophobic by quarternary ammonium cations was carried out. Quarternary ammonium cations increase the adsorption ability of organobentonite to organic pollutants with same hydrophobicity (Smith and Galan, 1995). The alkyl chains on the quarternary ammonium cations also create a partition medium for sorption of the organic pollutants (Smith and Galan, 1995).

The quarternary ammonium cations can be divided into two groups: 1) short-chain alkyl or aryl functional group, 2) long-chain functional group which is $(CH_3)_3$-N^+-R where R is a 10-, 12-, 14-, or 16-carbon alkyl chain. The first group consists of tetraethylammonium (TEA), benzyltrimethylammonium (BTMA), and benzyltriethylammonium (BTEA). The second group is decyltrimethylammonium (DTMA), dodecyltrimethylammonium (DDTMA), tetradecyltrimethylammonium (TDTMA), and hexadecyltrimethylammonium (HDTMA).

The quarternary ammonium cation is more hydrophobic with longer alkyl chain. The hydrophobicity consequently increases from short-chain alkyl or aryl functional group to long-chain functional group. For the long-chain functional group, the

hydrophobicity increases from DTMA, DDTMA, TDTMA to HDTMA. The structure of these quarternary ammonium cations can be seen in Figure 1.9 to Figure 1.15. Each of these quarternary ammonium cations contains only one nitrogen atom in its molecule. Hence the amount of quarternary ammonium cations that successfully added to bentonite was determined by carbon, hydrogen and nitrogen analyzer (CHN).

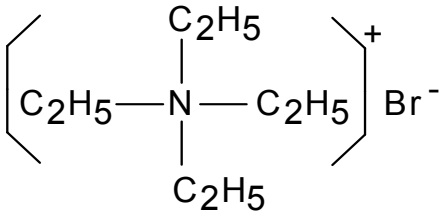


Figure 1.9 The structure of tetraethylammonium (TEA) bromide.

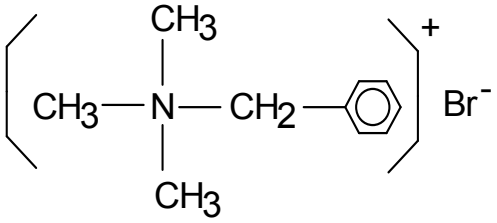


Figure 1.10 The structure of benzyltrimethylammonium (BTMA) bromide.

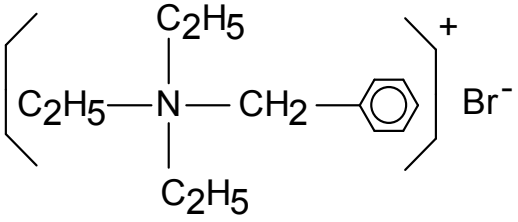


Figure 1.11 The structure of benzyltriethylammonium (BTEA) bromide.

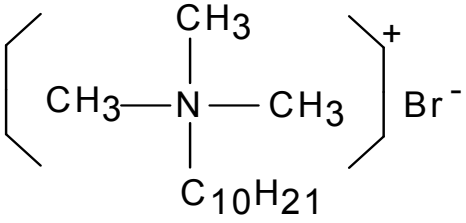


Figure 1.12 The structure of decyltrimethylammonium (DTMA) bromide.

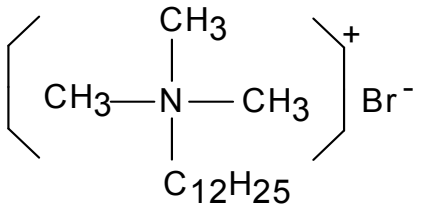


Figure 1.13 The structure of dodecyltrimethylammonium (DDTMA) bromide.

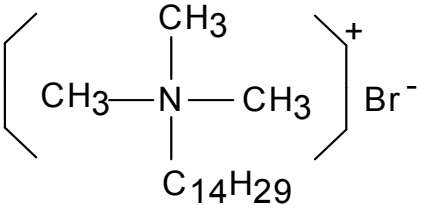


Figure 1.14 The structure of tetradecyltrimethylammonium (TDTMA) bromide.

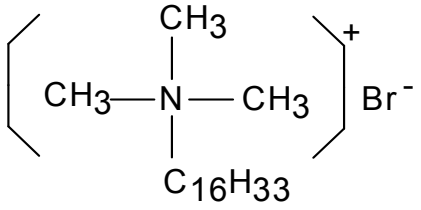


Figure 1.15 The structure of hexadecyltrimethylammonium (HDTMA) bromide.

1.5 Bentonite Modification

In this research, bentonite modification from hydrophilic to organophilic through ion exchange technique. The history of ion exchange can be traced back to Moses, who softened the bitter water of Mara to make it potable for his flock in the desert. Aristotle's observation indicated that the salt content of water is diminished or altered upon percolation through certain sands. The major evolution came in 1935 with the work of Adams and Holmes, two English scientists, whose chance discovery that a shattered phonograph record exhibited ion exchange properties led them to invent ion exchange resins, materials with in many respects superior properties (Helfferich, 1986).

According to Helfferich (1986), in the first decade after the Second World War, more stable and reproducible ion exchange resin on styrene basis and of strong-base anion exchangers (with quarternary ammonium groups) were advent. Then the commercial development of effective inorganic ion exchangers in the form of synthetic zeolites and macroporous type ion exchange resins were done. The macroporous type ion exchange resins opened up many applications under conditions where the active groups of conventional resins are not accessible for lack of swelling. Moreover, the resins are used as disinfectants. These resins have high sorption affinity for bacteria and carry antibacterial agents such as quarternary ammonium ions as either functional groups or counter ions.

The ion exchanger also acts as a carrier of a metal ion that forms complexes of different strengths with various ligands, and is used for the separations of such ligands. Ligand exchange becomes a standard chromatographic technique and is generally used for separations of amines, amino acids, etc. Ion exchange has been used widely in the field of catalysis (Helfferich, 1986). Ion exchange is then used in water treatment in this study.

According to Kunin (1958) in the crystal lattice theory, the ease with which the surface ions may be replaced by another ion depends therefore on: 1) the nature of the forces binding the ion to the crystal, 2) the concentration of the exchanging ion, 3) the charge of the exchanging ion, 4) sizes of the two ions, 5) the accessibility of lattice ions, and 6) solubility effects.

The lattice of the bentonite has to be large enough to permit an exchanging ion to diffuse into it. Bentonite has the ability to swell along its crystallographic c-axis when hydrated. The structure of bentonite is separated into two plates after the swelling, each consisting a silica layer and an alumina layer held together by the monovalent and divalent cations, such as sodium, potassium, calcium and magnesium. When hydrated, other cations may diffuse between the layers and exchange with these cations. The exchange capacity and the seat of exchange have been related to the constitution of the silicate lattice. If a silicon atom which has an ionic charge of four, is replaced with an aluminum atom that has the same coordination number but an ionic charge of three in the chains, the charge deficiency must be balanced by the presence of other cations.

This substitution explains the ion exchange phenomenon in bentonite. The substitution of a magnesium atom of an ionic charge of two for an aluminum atom of an ionic charge of three gives the same effects as the substitution of an aluminum atom for a silicon atom.

At high concentrations, the differences in the exchange 'potentials' of ions of different valence (Na^+ versus Ca^{2+}) diminish and, in some cases, the ion of lower valence has the higher exchange 'potential'. Organic ions of high molecular weight and complex metallic anionic complexes exhibit unusually high exchange potentials (Kunin, 1958).

According to Smith, *et al.* (1990), the layered structure of the clay allows expansion (swelling) after wetting, which in turn exposes additional mineral surface capable of cation adsorption. These factors, in combination with its small particle size, cause the montmorillonite to exhibit a high cation-exchange capacity relative to other natural soils. Therefore, bentonite which is a type of layered clay and composed primarily of Na^+-montmorillonite, is very suitable to be modified through ion exchange.

In aqueous systems, quarternary ammonium cations can be retained by both the outer and interlayer surfaces of an expandable clay particle by an ion-exchange process and are not easily displaced by smaller cations such as H^+, Na^+, or Ca^{2+}. The sorptive properties of the modified clay surface may be significantly altered by this substitution reaction.

The structure of bentonite in the middle of Figure 1.16 has been discussed earlier. As shown in Figure 1.16, quarternary ammonium cations were added to the internal and the external layers of the bentonite. The attraction of the organochlorine pesticides to quarternary ammonium cations is through the long hydrophobic chains (Delozier, *et al.*, 2002). The amount of organochlorine pesticides that has been attracted to the quarternary ammonium cations depends on the quantity of quarternary ammonium cations. The higher amount of quarternary ammonium cations found on the bentonite means more organochlorine pesticides can be eliminated from water through partitioning process by the alkyl chains of the quarternary ammonium cations.

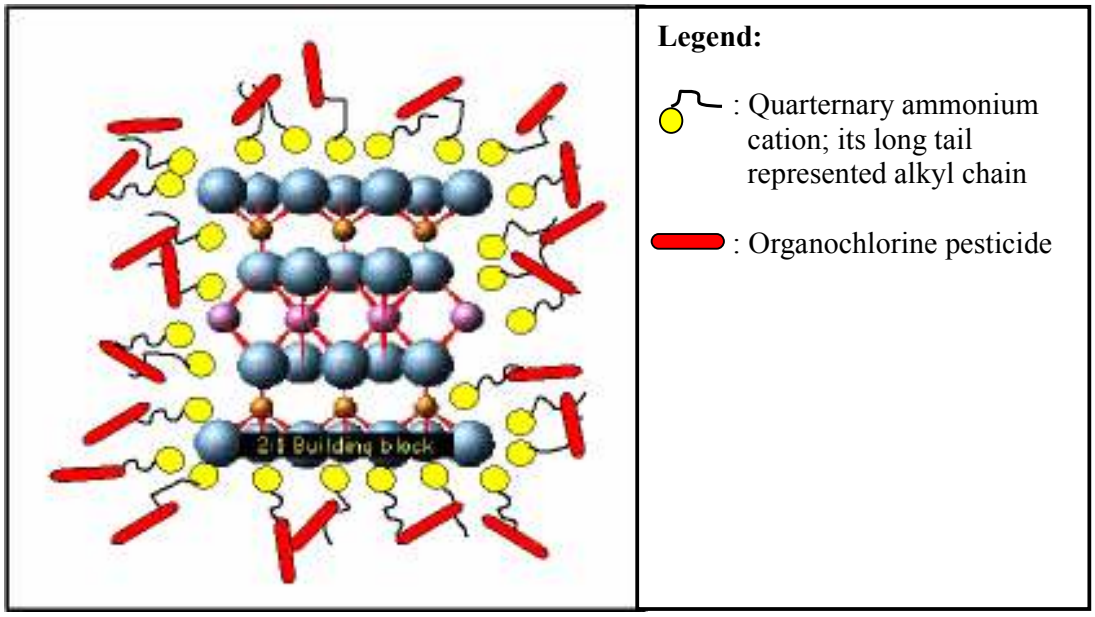


Figure 1.16 The diagram of removal of organochlorine pesticides from water by modified bentonite.

1.6 Water Quality Standards

Water quality standards are important guidelines to ensure that pollutants found in water do not exceed the safety level. In other words, these guidelines can be used to determine whether the water is safe for consumption or not. Global water quality standards and Malaysia water quality standards are used as guidelines in this research.

1.6.1 Global water quality standards

Water is transported globally in the environment, unconstrained by geopolitical boundaries through atmosphere, underground, oceans, waterways, human activities, life cycles of the flora and fauna. Environmental Health Laboratories (EHL) has suggested a set of drinking water quality standards as the global drinking water quality standards. The global water quality standards actually are a combination of drinking water quality standards from eleven organizations and developed countries: Environmental Health Laboratories of United States of America (EHL), United States Environmental Protection Agency (EPA), World Health Organization (WHO), Canadian Drinking

Water Quality Guidelines, Taiwan, Taipei Drinking Water Regulations, European Economic Community (EEC), United Nations, US EPA Contaminant Candidate List, South Africa, Umgeni, China and Czech Republic.

A few categories of the drinking water quality standards are divided as inorganics, disinfection by-products (DBPs), metals, radiological, solid organic chemicals (SOCs), volatiles, physical parameters, additional parameters and microbiological. Table 1.3 is the water quality standards of aldrin, dieldrin, DDT, heptachlor and mirex.

EHL (0.1 µg/L, 0.1 µg/L), WHO (0.03 µg/L, 0.03 µg/L), Canada (0.7 µg/L, 0.7 µg/L) and Taiwan (3 µg/L, 3 µg/L) have water quality standards for the concentrations of aldrin and dieldrin in drinking water. EHL, WHO, Canada, Taiwan and China set the safety consumption limit of the drinking water with the amount of DDT at 0.1 µg/L, 2 µg/L, 3 µg/L, 1 µg/L and 1 µg/L, respectively. EHL, WHO, EPA, Canada and Taiwan control the concentration of heptachlor in drinking water with 0.1 µg/L, 0.03 µg/L, 0.4 µg/L, 3 µg/L, and 1 µg/L, respectively. Only EHL (0.5 µg/L) has water quality standards for mirex in drinking water.

Table 1.3: A suggested global drinking water quality standards on the studied organochlorine pesticides.

SOCs-ug/L (ppb)	**Heptachlor**	**Aldrin**	**Dieldrin**	**DDT**	**Mirex**
BST	0.1	0.1	0.1	0.1	0.5
WHO	0.03	0.03	0.03	2	-
EPA	0.4	-	-	-	-
Canada	3	0.7	0.7	3	-
Taiwan	1	3	3	1	-
China	-	-	-	1	-
EPA Method (EHL-S125)	525.2	525.2	525.2	525.2	525.2
Note:-					
BST	Environmental Health Laboratories Broad Spectrum Test				
WHO	World Health Organization				
EPA	United States Environmental Protection Agency Regulated Analytes				
Canada	Canadian Drinking Water Quality Guidelines				
Taiwan	Taiwan, Taipei Drinking Water Regulations				
China	China				
EHL-S125	Environmental Health Laboratories – Gas Chromatography/Mass Spectrometry (GC/MS)				

1.6.2 Malaysian water quality standards

Interim National Water Quality Standards (INWQS) are developed for the Malaysian water quality standards. As shown in Table 1.4, water is divided into six classes (I, IIA, IIB, III, IV and V) by INWQS according to its uses.

Class I represents water bodies of excellent quality for the conservation of natural environment in its undisturbed state. Class IIA represents water bodies of good quality which mainly for raw water supply. Class IIB standard is based on criteria for recreational use and protection of sensitive aquatic species. Class III is defined with the primary objective of protecting common and moderately tolerant aquatic species of economic value. Class IV defines water required for major agricultural activities which may not cover minor applications to sensitive crops whereas Class V represents other water which do not meet any of the above uses.

Table 1.4: The classes of Malaysia's water according to the uses.

Class	Uses
l	Conservation of natural environment
	Water supply l - practically no treatment necessary (except by disinfection of boiling only) Fishery l - very sensitive aquatic species
llA	Water supply ll - conventional treatment required
	Fishery ll sensitive aquatic species
llB	Recreational use with body contact
lll	Water supply lll - extensive treatment required
	Fishery lll - common, of economic value and tolerant species
lV	Irrigation
V	None of the above

Table 1.5 showed the water condition parameter of INWQS. The water parameters of INWQS for inorganic residues are shown in Table 1.6.

Table 1.5: Interim National Water Quality Standards for Malaysia (INWQS) – Water Condition Parameter.

Parameters	(Units)	Classes					
		I	IIA	IIB	III	IV	V
Ammonical Nitrogen	mg/l	0.1	0.3	0.3	0.9	2.7	> 2
BOD	mg/l	1	3	3	6	12	> 12
COD	mg/l	10	25	25	50	100	> 100
DO	mg/l	7	5 - 7	5 - 7	3 - 5	< 3	< 1
pH	-	6.5-8.5	6.5-9.5	6 - 9	5 - 9	5 - 9	
Colour	TCU	15	150	150			
Electrical Conductivity	mmhos/ cm	1000	1000		-	6000	-
Floatables	-	N	N	N	-	-	-
Odour	-	N	N	N	-	-	-
Salinity	$^{o}/_{oo}$	0.5	1	-	-	-	-
Taste	-	N	N	N	-	-	-
Total Dissolved Solids	mg/l	500	1000	-	-	-	-
Total Suspended Solids	mg/l	25	50	50	150	300	> 300
Temperature	^{o}C	-	Normal +2	-	Normal +2	-	-
Turbidity	NTU	5	50	50	-	-	-
Faecal Caliform*	counts/ 100ml	10	100	400	5000 (2000)@	5000 (2000)	-
Total Coliform	counts/ 100ml	100	5000	50000	50000	50000	>50000

Note:-	
N	No visible floatable materials/debris
	or No objectionable odour
	or No objectionable taste
*	Geometric Mean
@	Maximum not to be exceeded

Table 1.6: Interim National Water Quality Standards for Malaysia (INWQS) – Inorganic Residues.

Parameters	(Units)	Classes				
		I	IIA / IIB	III[@]	IV	V
A1	mg/l	NATURAL LEVEL	-	(0.06)	0.5	LEVELS ABOVE IV
As	mg/l		0.05	0.4 (0.05)	0.1	
Ba	mg/l		1	-	-	
Cd	mg/l		0.01	0.01* (0.001)	0.01	
Cr(Vl)	mg/l		0.01	1.4 (0.05)	0.1	
Cr(lll)	mg/l		0.05	2.5	-	
Cu	mg/l		1	-	0.2	
Hardness	mg/l		250	-	-	
Ca	mg/l		-	-	-	
Mg	mg/l		-	-	-	
Na	mg/l		-	-	3 SAR	
K	mg/l		-	-	-	
Fe	mg/l		0.3	1	1 (leaf) 5 (others)	
Pb	mg/l		0.05	0.02* (0.01)	5	
Mn	mg/l		0.1	0.2	0.2	
Hg	mg/l		0.001	0.004 (0.0001)	0.002	
Ni	mg/l		0.05	0.9*	0.2	
Se	mg/l		0.01	0.25	0.02	
Ag	mg/l		0.05	0.0002	-	
Sn	mg/l		-	0.004	-	
U	mg/l		-	-	-	
Zn	mg/l		5	0.4*	2	
B	mg/l		1	(3.4)	0.8	
Cl	mg/l		200	-	80	
Cl_2	mg/l		-	(0.02)	-	
CN	mg/l		0.02	0.06 (0.02)	-	
F	mg/l		1.5	10	1	
NO_2	mg/l		0.4	0.4 (0.03)	-	
NO_3	mg/l		7	-	5	
P	mg/l		0.2	0.1	-	
Si	mg/l		50	-	-	
SO_4	mg/l		250	-	-	
S	mg/l		0.05	(0.001)	-	
Parameters	**(Units)**	**Classes**				
		I	**IIA / IIB**	**III[@]**	**IV**	**V**
CO_2	mg/l	Natural level	-	-	-	Levels above
Gross-a	Bq/l		0.1	-	-	

Gross-b	Bq/l		1	-	-	IV
Ra-266	Bq/l		< 0.1	-	-	
Sr-90	Bq/l		< 1	-	-	
Note:-						
@	Maximum (unbracketed) and 24-hour average (bracketed) concentrations					

Table 1.7 shows the water parameters of INWQS for organic residues. The water quality standards set the levels of organochlorine pesticides (aldrin/dieldrin, t-DDT, heptachlor) differently under INWQS according to water classes. The organochlorine pesticides in class I water are limited to their natural levels. Class IIA and IIB water have the same water quality standards for the organochlorine pesticides (aldrin/dieldrin, t-DDT, heptachlor) which are 0.02 mg/L, 0.1 mg/L and 0.05 mg/L, respectively. The maximum concentrations of the organochlorine pesticides (aldrin/dieldrin, t-DDT, heptachlor) for Class III water are 0.2 mg/L, 1 mg/L and 0.9 mg/L, respectively. Moreover, the average concentrations of the organochlorine pesticides (aldrin/dieldrin, t-DDT, heptachlor) for Class III water within 24 hours of discharge time should not be more than 0.01 mg/L, 0.01 mg/L and 0.06 mg/L, respectively. Specification of water quality standards on Class IV and V water was not done for the organochlorine pesticides.

Table 1.7: Interim National Water Quality Standards for Malaysia (INWQS) – Organic Residues.

Parameters	(Units)	Classes				
		I	IIA / IIB	III[@]	IV	V
CCE	m g/l	NATURAL LEVELS	500	-	-	LEVELS ABOVE IV
MBA/BAS	m g/l		500	5000 (200)	-	
O&G (mineral)	m g/l		40;N	N	-	
O&G (emulsified / edible)	m g/l		7000;N	N	-	
PCB	m g/l		0.1	6 (0.05)	-	
Phenol	m g/l		10	-	-	
Aldrin/Dieldrin	m g/l		0.02	0.2 (0.01)	-	
BHC	m g/l		2	9 (0.1)	-	
Chlordane	m g/l		0.08	2 (0.02)	-	
t-DDT	m g/l		0.1	1 (0.01)	-	
Endosulfan	m g/l		10	-	-	
Heptachlor/Epoxide	m g/l		0.05	0.9 (0.06)	-	
Lindane	m g/l		2	3 (0.4)	-	
2,4-D	m g/l		70	450	-	
2,4,5-T	m g/l		10	160	-	
2,4,5-TP	m g/l		4	850	-	
Paraquat	m g/l		10	1800	-	

Note:-	
N	Free from visible film, sheen, discoloration and deposits
@	Maximum (unbracketed) and 24-hr average (bracketed) concentrations

On the other hand, the sewage and industrial effluents are being identified under Environmental Quality (Sewage and Industrial Effluents) Regulations 1979. In Table 1.8, the effluents discharge from a sewage treatment process to an inland water are identified by two types of water quality standards according to the location of discharge. Standard A criteria applies only to catchments areas located upstream of drinking water supply off-takes while the discharges into other inland water are categorized under Standard B.

Table 1.8: Parameter limits of effluent from Environmental Quality (Sewage and Industrial Effluents) Regulations 1979 [Regulations 8(1), 8(2), 8(30].

Parameters	Units	Classes	
		A	B
Temperature	^{o}C	40	40
pH Value	-	6.0 - 9.0	5.5 - 9.0
BOD_5 at $20^{o}C$	mg/l	20	50
COD	mg/l	50	100
Suspended Solids	mg/l	50	100
Mercury	mg/l	0.005	0.05
Cadium	mg/l	0.01	.02
Chromium, Hexalent	mg/l	0.05	0.05
Arsenic	mg/l	0.05	0.10
Cynide	mg/l	0.05	0.10
Lead	mg/l	0.10	0.5
Chromium, Trivalent	mg/l	0.20	1.0
Copper	mg/l	0.20	1.0
Mangenese	mg/l	0.20	1.0
Nickel	mg/l	0.20	1.0
Tin	mg/l	0.20	1.0
Zinc	mg/l	1.0	1.0
Boron	mg/l	1.0	4.0
Iron (Fe)	mg/l	1.0	5.0
Phenol	mg/l	0.001	1.0
Free Chlorine	mg/l	1.0	0.5
Sulphide	mg/l	0.50	0.05
Oil and Grease	mg/l	Not detactable	10.0

Note:-	
Standard A	for discharge into inland waters in a catchment
	or No objectionable odour
Standard B	for discharges into other inland waters

REFERENCES

Akbal, F. Ö., Akdemir, N. and Onar, A. N. (2000). FT-IR Spectroscopic Detection of Pesticide after Sorption onto Modified Pumice. *Talanta.* 53: 131-135.

Albanis, T. A. and Hela, D. G. (1995). Multi-Residue Pesticide Analysis in Environmental Water Samples Using Solid-Phase Extraction Disc and Gas Chromatography with Flame thermionic and Mass-Selective Detection. *Journal of Chromatography A*. 707: 283-292.

Balci, S. and Gökçay, E. (2002). Effects of Drying Methods and Calcinations Temperatures on The Physical Properties of Iron Intercalated Clays. *Materials Chemistry and Physics.* 76: 46-51.

Banat, F. A., Al-Bashir, B., Al-Asheh, S. and Hayajneh, O. (2000). Adsorption of Phenol by Bentonite. *Environmental Pollution*. 107: 391-398.

Barrow, G. M. (1996). *Physical Chemistry*. 6th ed. United States of America: The McGraw-Hill Companies, Inc. 654-666.

Bibleman, T. F. and Falconer, R. L. (1999). Using Enantiomers To Trace Pesticide Emissions. *Environ. Sci. Technol*. 33 (9): 206A-209A.

Bolto, B., Dixon, D., Eldridge, R. and King, S. (2000). Cationic Polymer and Clay or Metal Oxide Combinations for Natural Organic Matter Removal. *Wat. Res*. 35: 2669-2676.

Bors, J., Dultz, St. and Riebe, B. (1999). Retention of Radionuclides by Organophilic Bentonite. *Engineering Geology*. 54: 195-206.

Bottero, J. Y., Khatib, K., Thomas, F., Julker, K., Bersilon, J. L. and Malevialle, J. (1994). Adsorption of Atrazine onto Zeolites and Organoclays in The Presence of Background Organics. *Water Res.* 28: 483-490.

Boyd, S. A., Mortland, M. M. and Chiou, C. T. (1988). Sorption Characteristics of Organic Compounds on Hexadecyltrimethylammonium-smectite. *Soil Sci. Soc. Am. J.* 52: 652-657.

Braun, R. D. (1982). *Introduction to Chemical Analysis*. United States of America: McGraw-Hill, Inc. 394-419.

Cadena, F. (1989). Use of Tailored Bentonite for Selective Removal of Organic Pollutants. *Journal of Environmental Engineering*. 115: 756-767.

Cadena, F. and Cazares, E. (1996). *Clay Mineral Society Workshop Lectures.* 8: 69-94.

Caňizares, P., Valverde, J. L., Sun Kou, M. R. and Molina, C. B. (1999). Synthesis and Characterization of PILCs with Single and Mixed Oxide Pillars Prepared from Two different Bentonites. A Comparative Study. *Microporous and Mesoporous Materials.* 29: 267-281.

Celis, R., Cornejo, J., Hermosin, M. C. and Koskinen, W. C. (1997). Sorption-Desorption of Atrazine and Simazine by Model Soil Colloidal Components. *Soil Sci. Soc. Am. J.* 61: 436-443.

Chegrouche, S., Mellah, A. and Telmoune, S. (1997). Removal of Lanthanum from Aqueous Solutions by Natural Bentonite. *Wat. Res*. 31: 1733-1737.

Claver, C., Fernández, E., Margalef-Català, R., Medina, F., Salagre, P. and Sueiras†, J. E. (2001). Studies on the Characterization of Several Iridium- and Rhodium-clay Catalysts and Their Activity in Imine Hydrogenation. *Journal of Catalysis.* 201: 70-79.

Cox, L., Hermosin, M. C. and Cornejo, J. (1994). Interactions of Methomyl with Montmorillonite. *Clay Minerals*. 29: 767-774.

Cox, L., Hermosin, M. C. and Cornejo, J. (1995). Adsorption Mechanisms of Thuiazafluron by Mineral Soil Clay Components. *Europ. J. Soil Sci.* 46: 431-438.

Cullity, B. D. (1978). *Elements of X-Ray Diffraction.* 2nd ed. Menlo Park, CA: Addison-Wesley.

Deitsch, J. J., Smith, J. A., Culver, T. B., Brown, R. A. and Riddle, S. A. (2000). Distributed-Rate Model Analysis of 1,2-Dichlorobenzene Batch Sorption and Desorption Rates for Five Natural Sorbents. *Environ. Sci. Technol.* 34: 1469-1476.

Delozier, D. M., Orwoll, R. A., Cahoon, J. F., Johnston, N. J., Smith Jr, J. G. and Connell, J. W. (2002). Preparation and Characterization of Polyimide/Organoclay Nanocomposites. *Polymer.* 43: 813-822.

Dentel, S. K., Bottero, J. Y., Khatib, K., Demougeot, H., Diguet, J. P. and Anselme, C. (1995). Sorption of Tannic Acid, Phenol and 2,4,5-trichlorophenol on Organoclays. *Water Res.* 29: 1273-1280.

EPA. (1998). Permeable Reactive Barrier Technologies for Contaminant Remediation. U. S. EPA Remedial Technology Fact Sheet, EPA 600/R-98/125: 102.

Falaras, P. and Petridis, D. (1992). Incorporation of Anionic Species in Organoclay-Modified Electrodes. *J. Electroanal. Chem.* 337: 229-239.

Fatoki, O. S. and Awofolu, R. O. (2003). Methods for Selective Determination of Persistent Organochlorine Pesticide Residues in Water and Sediments by Capillary Gas Chromatography and Electron-Capture Detection. *Journal of Chromatography A*. 983: 225-236.

Feldkamp, J and White, J. L. (1978). Protonation of Bases in Clay Suspensions. In *Proc. Int. Clay Conf.* 1978. Oxford: Developments in Sedimelology. 27: 187-196.

Fritz, J. S. (1999). *Analytical Solid-Phase Extraction*. 1st ed. United States of America: John Wiley & Sons, Inc. 63-71.

Gavaskar, A. R., Gupta, N., Sass, B. M., Janosy, R. J., O'Sullivan, D. (1998). *Permeable Barriers for Groundwater Remediation*. Columbus: Batelle Press. 176.

Gillman, G.P. and Sumpter, E.A. (1986). Modification to the Compulsive Exchange Method for Measuring Exchange Characteristics of Soils. *Aust. J. Soil Res*. 24: 61-66.

Gitipour, S., Bowers, M. T. and Bodocsi, A. (1997). The Use of Modified Bentonite for Removal of Aromatic Organics from Contaminated Soil. *J. Coll. Interface Sci.* 196: 191-198.

Gonzalez-Pradas, E., Villafranca-Sanchez, M., Gallego-Campo, A., Ureña-Amate, D. and Fernandez-Perez, M. (1996). Removal of Atrazine from Aqueous Solution by Natural and Activated Bentonites. *J. Environ. Qual.* 26: 1288-1291.

Gonzalez-Pradas, E., Villafranca-Sanchez, M., Socias-Viciana, M. M., Castillo-Sanchez, J. and Fermandez-Perez, M. (1993). Removal of 3-(3,4-dichlophenyl)-1,1-

dimethylurea from Aqueous Solution by Natural and Activated Bentonites. *J. Chem. Tech. Biotechnol.* 52: 221-228.

Griffiths, P. R. and Haseth, J. A. (1986). *Fourier Transform Infrared Spectrometry*. United States of America: John Wiley & Sons, Inc. 166-425.

Güngör, N. and Karaoğlan, S. (2001). Interactions of Polyacrylamide Polymer with Bentonite in Aqueous Systems. *Materials Letters*. 48: 168-175.

Haggerty, G. M. and Bowman, R. S. (1994). Sorption of Inorganic Anions by Organo-Zeolites. *Environ. Sci. Technol*. 28: 452-458.

Halsall, C. J., Stern, G. A., Barrie, L. A., Fellin, P., Muir, D. C. G., Billeck, B. N., Rovinsky, F. Ya., Kononov, E. Ya. and Pastukhov, B. (1998). Multi-year Observations of Organohalogen Pesticides in The Arctic Atmosphere. *Environ. Pollut*. 102 (1): 51-62.

Harper, M. and Purnell, C. J. (1990). Alkylammonium Montmorillonites as Adsorbents for Organic Vapors from Air. Environ. Sci. Technol.. 24 (1): 62-66.

Helfferich, F. G. (1986). Ion Exchange: Past, Present, and Future. In. *Rodrigues, A. E. Ion Exchange: Science and Technology*. The Netherlands: Martinus Nijhoff Publishers, Dordrecht. 23-32.

Hermosin, M. C. and Cornejo, J. (1992). Removing 2,4-D from Water by Organo-Clays. *Chemosphere.* 24: 1492-1497.

Hermosin, M. C., Crabb, A. and Cornejo, J. (1995). Sorption Capacity of Organo-Clays for Anionic and Polar Organic Contaminants. *Fresenius Environ Bull.* 4: 514-519.

Hermosin, M. C., Roldan, I. and Cornejo, J. (1991). Binding Mechanisms of Maleic Hydrazide to Homoionic Montmorillonites. *The Sci. Total Environ*. 123/124: 109-119.

Hillel, D. (1980). *Fundamentals of Soil Physic*. New York: Academic Press.

Huttenloch, P., Roehl, K. E. and Czurda, K. (2001). Sorption of Nonpolar Aromatic Contaminants by Chlorosilane Surface Modified Natural Minerals. *Environ. Sci. Technol.* 35: 4260-4264.

Ichikawa, Y., Kawamura, K., Nakano, M., Kitayama, K., Seiki, T. and Theramast, N. (2001). Seepage and Consolidation of Bentonite Saturated with Pure- or Salt-Water

by the Method of Unified Molecular Dynamics and Homogenization Analysis. *Engineering Geology*. 60: 127-138.

Jaynes, W. F. and Boyd, S. A. (1991a). Clay Minerals Type and Organic Compound Sorption by Hexadecyltrimethylammonium-Exchanged Clays. *Soil Sci. Soc. Am. J.* 55: 43-48.

Jaynes, W. F. and Boyd, S. A. (1991b). Hydrophobicity of Siloxane Surfaces of Smectites as Revealed by The Aromatic Hydrocarbon Adsorption from Waters. *Clays & Clay Minerals.* 39: 426-436.

Jones, K. C. (Editor). (1998). Air-surface Exchange of Persistent Organic Pollutants. *Environ. Pollut*. 102 (1).

Kamei, G., Oda, C., Mitsui, S., Shibata, M. and Shinozaki, T. (1999). Fe(II)-Na Ion Exchange at Interlayers of Smectite: Adsorption-Desorption Experiments and a Natural Analogue. *Engineering Geology*. 54: 15-20.

Koh, S. and Dixon, J. B. (2001).Preparation and Application of Organo-Minerals as Sorbents of Phenol, Benzene and Toluene. *Appl. Clay Sci.* 18 (3): 111-122.

Kunin, R. (1958). *Ion Exchange Resins.* 2nd ed. United States of America: John Wiley & Sons, Inc. 6-33.

Lagaly, G. (1994). Bentonites: Adsorbent of Toxic Substances. *Prog. Colloid & Polym. Sci.* 95: 61-72.

Lagaly, G. and Weiss, A. (1969). Determination of The Layer Charge of Mica-Type Layer Silicates. In *Proc. Int. Clay Conf*. 1969. Tokyo: L. Heller (ed.), Israel University Press. 1: 61-80.

Laird, D. A. (1996). Interactions Between Atrazine and Smectite Surfaces. *ACS Symp. Serie*. 630: 86-100.

Lee, D., Lee, S. H., Char, K. and Kim, J. (2000). Expansion Distribution of Basal Spacing of the Silicate Layers in Polyaniline/Na^+-Montmorillonite Nanocomposites Monitored with X-ray Diffraction. *Macromol. Rapid Commun.* 21: 1136-1139.

Lee, J. F., Crum, J. R. and Boyd, S. A. (1989). Enhanced Retention of Organic Contaminants by Soils Exchanged with Organic Cations. *Environ. Sci. Technol*. 23: 1365-1372.

Lenarda, M., Storaro, L., Ganzerla, R. and Bertoncello, R. (1999). Synthesis, Characterization and Catalytic Activity of Ruthenium Containing Aluminium Pillared Bentonites. *Journal of Molecular Catalysis.* 144: 151-158.

Li, Z. and Bowman, R. S. (1998). Sorption of Perchloroethylene by Surfactant-Modified Zeolite as Controlled by Surfactant Loading. *Environ. Sci. Technol*. 32: 2278-2282.

Li, Z. and Bowman, R. S. (2001). Retention of Inorganic Oxyanions by Organo-Kaolinite. *Wat. Res*. 35: 3771-3776.

Li, Z., Burt, T. and Bowman, R. S. (2000). Sorption of Ionizable Organic Solutes by Surfactant-Modified Zeolite. *Environ. Sci. Technol.* 34: 3756-3760.

Li, Z., Jones, H. K., Bowman, R. S. and Helferich, R. (1999). Enhanced Reduction of Chromate and PCE by Pelletized Surfactant-Modified Zeolite/Zero Valent Iron. *Environ. Sci. Technol.* 33: 4323-4330.

Lo, I. M. C., Lee, C. H. and Liljestrand, H. M. (1996). Tricaprylmethylammonium Bentonite Compexes As Adsorbents for Benzene, Toluene, Ethylbenzene and Xylene. *Wat. Sci. Tech.* 34: 319-325.

McFadden, W. (1973). *Techniques of Combined Gas Chromatography/Mass Spectrometry: Applications in Organic Analysis*. United States of America: John Wiley & Sons Inc. 8-329.

Mellah, A. and Chegroushe, S. (1997). The Removal of Zinc from Aqueous Solutions by Natural Bentonite. *Wat. Res*. 31: 621-629.

Mercier, M. (1981). *Criteria (Dose/Effect Relationships) for Organochlorine Pesticides*. Great Britain: A. Wheaton & Co. Ltd. 59-100.

Mortland, M. M. (1970). Clay-Organic Interactions. *Adv. Agron*. 22: 75-117.

Mortland, M. M., Shaobai, S. and Boyd, S. A. (1986). Clay-Organic Complexes as Adsorbents for Phenol and Chlorophenols. *Clays & Clay Minerals.* 34: 581-587.

Naseem, R. and Tahir, S. S. (2001). Removal of Pb(II) from Aqueous/Acidic Solutions by Using Bentonite as An Adsorbent. *Wat. Res*. 35: 3982-3986.

Ockenden, W. A., Steinnes, E., Parker, C. and Jones, K. C. (1998a). Observation on Persistent Organic Pollutants (POPs) in Plants: Implications for Their Use as Passive Air Samplers and for Global POPs Cycling. *Environ. Sci. Technol*. 32: 2721-2726.

Ockenden, W. A., Sweetman, A., Prest, H. F., Steinnes, E. and Jones, K. C. (1998b). Toward an Understanding of The Global Atmospheric Distribution of Persistent Organic Pollutants: The Use of Semi-Permeable Membrane Devices as Time Integrated Passive Samplers. *Environ. Sci. Technol*. 32. 2795-2803.

Piver, W. T. (1992). Contamination and Restoration of Groundwater Aquifers. *Environ. Health Perspec.* 100: 237-247.

Ritter, L., Solomon, K. R., Forget, J., Stemeroff, M. and O'Leary, C. (1999). An Assessment Report on DDT, Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, Polychlorinated Biphenyls, Dioxins and Furans in *the International Programme on Chemical Safety (IPCS) within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC)*. 1-43.

Ross, D.S. (1995). Recommended methods for determining soil cation exchange capacity. In. *Recommended Soil Testing Procedures for the Northeastern United States.* University of Delaware Ag. Experiment Station Bulletin no. 493, second edition. 62-69.

Reid, B. J., Semple, K. T. and Jones, K. C. (1998). Prediction of Bioavailability of Persistent Organic Pollutants by a Novel Extraction Technique. In *Proceedings of CONSOIL '98: The Sixth International FZK/TNO Conference on Contaminated Soil*. 1998. London: Thomas Telford Publishing, 2: 889-890.

Rožić, M., Cerjan-Stefanović, Š., Kurajica, S., Vančina, V. and Hodžić, E. (2000). Ammonical Nitrogen Removal from Water by Treatment with Clays and Zeolites. *Wat. Res.* 34: 3675-3681.

Settle, F. A. (1997). *Handbook of Instrumental Techniques for Analytical Chemistry.* 1st ed. United States of America: Prentice-Hall, Inc. 247-277, 339-357, 609-624.

Shen, Yun-Hwei. (2002). Removal of Phenol from Water by Adsorption-flocculation Using Organobentonite. *Water Research*. 36: 1107-1114.

Smith, J. A. and Galan, A. (1995). Sorption of Nonionic Organic Contaminants to Single and Dual Organic Cation Bentonites from Water. *Environ. Sci. Technol.* 29 (3): 685-692.

Smith, J. A. and Jaffé, P. R. (1994). Adsorptive Selectivity of Organic-Cation-Modified Bentonite for Nonionic Organic Contaminants. *Water, Air and Soil Pollution.* 72: 205-211.

Smith, J. A., Jaffẽ, P. R. and Chiou, C. T. (1990). Effect of Ten Quarternary Ammonium Cations on Tetrachloromethane Sorption to Clay from Water. *Environ. Sci. Technol.* 24 (8): 1167-1172.

Socias-Viciana, M. M., Hermosin, M. C. and Cornejo, J. (1998). Removing Prometrone from Water by Clays and Organic Clays. *Chemosphere.* 37 (2): 289-300.

Spencer, W. F., Singh, G., Taylor, C. D., LeMert, R. A., Cliath, M. M. and Farmer, W. J. (1996). *J. Environ. Qual*. 25: 815-821.

Srimurali, M., Pragathi, A. and Karthikeyan, J. (1998). A Study on Removal of Fluorides from Drinking Water by Adsorption onto Low-Cost Materials. *Environmental Pollution*. 99: 285-289.

Stock, R. and Rice, C. B. F. (1974). *Chromatographic Methods*. 3rd ed. London, Great Britain: Chapman and Hall Ltd. 177-278.

Terence, H. C. (2003). *Clay Minerals*. United States of America: Department of Soil, Water, and Climate, University of Minnesota. Chapter 12.

Thermo Finnigan Italia. (2001). *FlashEA™ 1112 Elemental Analyzer Operating Manual.* 3rd ed. Italy: Thermo Finnigan Italia, Technical Publications. 11-15, 115-169.

Valverde, A., Pihlström, T. and Andersson, A. (1997). Analysis of Pyraclofos in Crops by the Swedish National Food Administration Gas Chromatographic Multiresidue Methodology. *Analytica Chimica Acta*. 338: 63-68.

Yalçin, T., Alemdar, A., Ece, Ö. I., Güngör, N. and Çoban, F. (2002). By Particle Interactions and Rheological Properties of Bentonite + ALS Suspensions. *Materials Letters*. 53: 211-215.

Zhang, Z. Z., Sparks, D. L. and Scriver, N. C. (1993). Sorption and Desorption of Quarternary Amine Cations on Clay. *Environ. Sci. Technol.* 27: 1625-1631.